Research on the Size and Shape of Large
Molecules and Colloidal Particles

Technical Report No. 4

The Determination of Spherical Particle
Size Distributions from Turbidity Spectra.

By

A. F. Stevenson
Depts. of Mathematics and Physics
Wayne University

Submitted by

W. Heller
Dept. of Chemistry
Wayne University

1. Introduction

Previous technical reports have dealt with light scattering by a single spherical particle, or by a mono-disperse system of such particles. When the scattering by a hetero-disperse system of particles is used to determine the particle size distribution, we are concerned with the determination of an unknown function. To determine such a function completely, it is evidently necessary to observe some quantity which depends on a parameter which can be varied continuously. Two such parameters immediately suggest themselves: the wave-length of the light and the angle of observation. In this report only the first of these is considered, and attention is focussed on the question of what can be determined as to particle size distribution from turbidity measurements when the wave-length is varied. It is assumed throughout that the scattering particles are all spherical in shape and of the same refractive index (independent of the wave-length), and that the concentration is sufficiently low for multiple scattering to be neglected.

2. The integral equation for the distribution function and its solution.

The scattering cross-section for a single spherical particle of radius x when illuminated by monochromatic light of wave-length λ can be written in the form

$$\sigma = \frac{\lambda^2}{2\pi} f(kx),$$

$$(1)$$

where $k = 2\pi/\lambda$,

and f is a function which has been extensively tabulated.[1] It depends on the

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[1]See, for instance, Technical Reports 1, 2, 3 of this series; Tables of Scattering Functions for Spherical Particles, National Bureau of Standards (Washington, 1948); R. O. Gumprecht and C. M. Sliepcevitch, Tables of light-scattering Functions for Spherical Particles, (University of Michigan, 1951). The function f is identical with the function Σ of Technical Report No. 1. In terms of the scattering coefficient K, $f(\alpha) = \frac{\alpha^2}{2} K(\alpha)$, where $\alpha = kx$.

refractive index m as well as on k; we shall, however, omit the dependence on m.

Let the number of scattering particles per unit volume with radii in the range $(x, x + dx)$ be $n(x) \, dx$, and let the turbidity at wave-length λ be denoted by $\tau(\lambda)$. Neglecting multiple scattering, we then have

$$F(k) = \int_0^\infty f(kx)\, n(x)\, dx, \tag{2}$$

where

$$F(k) = \frac{2\pi}{\lambda^2}\, \tau(\lambda). \tag{3}$$

The problem is, then, to solve the integral equation (2) for the function $n(x)$, the function $F(k)$ and the kernel $f(kx)$ being regarded as known.

If we suppose that $F(k)$ is known for all values of k from 0 to ∞ (i.e. $\tau(\lambda)$ is known for all wave-lengths from 0 to ∞), then (2) is of a type for which a rigorous solution is possible by Mellin transforms.[2] Unfortunately, however, this solution is of little practical use in the present case. For in practice the turbidity, and hence $F(k)$, will only be known for quite a limited range of k, a range not sufficient to determine the Mellin transform of $F(k)$. Further, even if $F(k)$ were known for a sufficiently wide range of k, it would then be necessary to take account of the variation of refractive index with wave-length, and this would destroy the special form of the equation (2). A further objection is that the Mellin transform solution would require fairly extensive numerical computation.

Various other methods of solving (2) were therefore considered. In one of these, it was assumed that the distribution was narrow, about some mean radius x_0

[2] See, for instance, E. C. Titchmarch, Introduction to the Theory of Fourier Integrals, (Oxford, 1948), 316.

say, and a Taylor series for the function $f(kx)$ in the neighborhood of kx_0 was used, the derivatives of the function f being found numerically. The calculation of the higher derivatives proved unsatisfactory, however, owing to irregular differences in the tabulated function.

Further, this method would be of no use for a broad distribution, and was therefore abandoned.

Another method attempted was to replace the integral equation (2) by a set of linear equations. The requisite matrix inversion was performed by the Wayne Computation Center. This method also proved unsatisfactory, due to the fact that some of the elements of the inverse matrix were very large compared with others, so that, as the function $F(k)$ in (2) is, in practice, subject to experimental errors, the results deduced in this way would be unreliable. This behavior of the inverse matrix is evidently connected with the fact that the function f is a rapidly increasing function of its argument (see on).

The method finally adopted was the following. Although it has not yet been brought to a numerical conclusion, it is believed that it should give reliable results subject to certain restrictions on the distribution function. In the first place, we shall suppose that the particle radii lie within a certain range, say

$$x_0 - \Delta x \leq x \leq x_0 + \Delta x, \tag{4}$$

and that observations of turbidity are made at wave-lengths also lying within a certain range, say

$$k_0 - \Delta k \leq k \leq k_0 + \Delta k. \tag{5}$$

We must then write (2) in the form

$$F(k) = \int_{x_0 - \Delta x}^{x_0 + \Delta x} f(kx)\, n(x)\, dx, \tag{6}$$

where $k_0 - \Delta k \leq k \leq k_0 + \Delta k$.

Let us now make the substitutions:

$$x = x_o + \Delta x \cdot x', \tag{7}$$

$$k = k_o + \Delta k \cdot k'; \tag{8}$$

then (6) can be written:

$$\psi(k') = \int_{-1}^{1} \psi(k', x') N(x') dx', \quad (-1 \leq k' \leq 1), \tag{9}$$

where

$$\phi(k') = F(k), \tag{10}$$

$$\psi(k', x') = f(kx), \tag{11}$$

$$N(x') = n(x) \Delta x. \tag{12}$$

We observe that $N(x')dx'$ is the number of particles per unit volume with radii between

$$x_o + \Delta x \cdot x' \quad \text{and} \quad x_o + \Delta x (x' + dx').$$

Let us now suppose that the kernel $\psi(k', x')$ is expanded in a series of Legendre polynomials:

$$\psi(k', x') = \sum_{i,j=0}^{\infty} c_{ij} P_i(k') P_j(x'). \tag{13}$$

Multiplying (9) by $P_i(k')$ and integrating with respect to k' from -1 to 1, we obtain:

$$\sum_{j=0}^{\infty} c_{ij} N_j = \frac{2i+1}{2} \int_{-1}^{1} \phi(k') P_i(k') dk', \tag{14}$$

where

$$N_j = \int_{-1}^{1} N(x') P_j(x') dx'. \tag{15}$$

Equations (14) now constitute an infinite set of linear equations for the determination of the unknown constants N_j. Having found these, $N(x')$ is given by

$$N(x') = \sum_{j=0}^{\infty} N_j P_j(x'). \tag{16}$$

In practice, of course, a finite number of terms in (13), (14), (16) must be used.

Any system of orthogonal functions could be used in place of the Legendre polynomials. These particular functions are suggested, however, by the fact that the function f can be well approximated over a fairly wide range of its argument by a polynomial of fairly low degree, say of degree p. Taking account of (7), (8), (11), this means that $\psi(k^1, x^1)$ can be approximated by a polynomial which is of degree p in each of the variables k^1, x^1, and hence by using only Legendre polynomials of degree $\leq$ p in (13). With this approximation, (14) becomes a set of (p + 1) equations in (p + 1) unknowns. For the ranges of particle size and wave-length so far considered, p could be quite a small number—say from 3 to 5. Whether a rather small number of terms in the series (16) yields a good approximation to the true distribution function depends, of course, on the nature of this function and, specifically, on whether it can be well approximated by a polynomial of low degree. The trend of the values of the coefficients N_j should give a fairly good indication as to the rapidity of convergence of the series (16).

Irrespective of the convergence of (16), however, a knowledge of a certain number of the coefficients N_j provides us with useful information about the distribution function. For, from (7), (12) and (15), we see that if the first (p + 1) coefficients η_j are known, then the first (p + 1) moments of the distribution with respect to the origin, namely

$$M_j = \int_{x_0 - \Delta x}^{x_0 + \Delta x} n(x) \, x^j \, dx \quad (i = 0, 1, \cdots, p), \tag{17}$$

can be found. The moment M_0 gives the total number of particles, while M_1/M_0 gives the mean radius of the particles. Higher moments furnish the mean square deviation, mean cubic deviation, and so on, so that considerable information as to the nature of the distribution can be obtained in this way.

If it is desired only to calculate the moments M_j, when the function f is approximated by a polynomial, the above procedure may be shortened as follows: let

us write, as an approximation,

$$f(kx) = \sum_{j=0}^{k} c_j (kx)^j.$$

Then substituting this in (6) and proceeding as before, we obtain

$$\sum_{j=0}^{k} a_{ij} M_j = \int_{-1}^{1} \phi(k') P_i(k') dk',$$ (18)

where

$$a_{ij} = c_j \int_{-1}^{1} (k_0 + \Delta k \cdot k')^j P_i(k') dk'.$$ (19)

Equations (18) are a set of $(p + 1)$ equations to determine the $(p + 1)$ moments M_0, M_1, ..., M_p. The coefficients a_{ij} can be calculated once and for all. The integrals occurring in (18) (or (14)) can be calculated by numerical integration from the observed turbidity or -- perhaps rather more simply -- by approximating the function $\phi(k')$ by a polynomial in k^1 and then expressing the various powers of k^1 in terms of Legendre polynomials. Since, from (19), $a_{ij} = 0$ if $i > j$, the equations (18) can be solved without difficulty. An experimental check can be obtained from the value of the moment M_3. For the total mass per unit volume of the scattering particles is $\frac{4}{3}\pi \rho M_3$, where ρ is the density of the particle material, and this quantity will be known or can be determined.

In connection with this method, the following point should be observed: the function f is a rapidly increasing function of its argument over the useful range, especially for small values of the argument ($f(\alpha) \sim const \cdot \alpha^b$ for $\alpha \ll 1$), which means that the larger particles contribute much more to the scattering than the smaller ones. Consequently, owing to the experimental errors in the determination of turbidity, it will not be possible to determine accurately the distribution function for the smaller values of x if the distribution is a broad one. The moments M_j should, nevertheless, be given with fair accuracy.

Another related point is the following: although the function f can be well approximated by a polynomial of low degree over a useful range of its argument,

such a representation gives a large percentage error (though a small absolute error) for small values of the argument (assuming that small values of the argument have to be used, which is the case if the lower limit of particle radii is small). This will not matter if the distribution is a broad one. If, however, the distribution is such that an appreciable fraction of the relevant values of kx are small, the results obtained will be misleading. To take an extreme case, if the approximation $\frac{}{}(kx) = const.(kx)^6$ (Rayleigh scattering) is valid over the whole relevant range of values of kx, then evidently all that can be determined about the distribution is the value of the moment M_6.

It is hoped to issue a further report shortly where numerical data will be given which will enable the method to be carried through explicitly and without too much labor. It is hoped also to present comparisons of particle size distributions obtained from turbidity measurements with those obtained electron-microscopically.

3. Conclusion.

It should be possible to determine the first few moments of the particle radius distribution from turbidity measurements with fair accuracy, provided that not too wide limits can be set to the particle radii, and that not too large a fraction of the particles have ''small'' radii. From these moments the distribution itself can be calculated if the series of Legendre polynomials (16) is sufficiently rapidly convergent.